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TUTORIAL REVIEW

Design of magnetic coordination complexes for quantum computing

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A very exciting prospect in coordination chemistry is to manipulate spins within magnetic complexes for the realization of quantum logic operations. An introduction to the requirements for a paramagnetic molecule to act as a 2-qubit quantum gate is provided in this *tutorial review*. We propose synthetic methods aimed at accessing such type of functional molecules, based on ligand design and inorganic synthesis. Two strategies are presented: (i) the first consists in targeting molecules containing a pair of well-defined and weakly coupled paramagnetic metal aggregates, each acting as a carrier of one potential qubit, (ii) the second is the design of dinuclear complexes of anisotropic metal ions, exhibiting dissimilar environments and feeble magnetic coupling. The first systems obtained from this synthetic program are presented here and their properties are discussed.

1 Introduction

One of the most difficult challenges in nanoscience is the physical implementation of quantum computing (QC), which aims at using the laws of quantum mechanics to perform the tasks of information processing.[1] The basic element of information in classical computation is the *bit*, which can take two values (*e.g.* 1 and 0). Its material realization is a classical physical system with two well defined states. In contrast, the QC counterpart is a quantum system termed *qubit* with quantum microstates that can be either $|1\rangle$ or $|0\rangle$, but also any arbitrary superposition of these two (namely, $|\varphi\rangle = \alpha|0\rangle + \beta|1\rangle$, see Fig. 1, left). The "quantum parallelism", associated with the use of such superpositions, is expected to enormously increase the potential of information processing[2–4] if it becomes possible to reliably extract and manipulate this information from a quantum system.

QC operations are performed by logic quantum gates (QGs). The simplest of these are single qubit unitary rotations which, starting from a basis state, say $|1\rangle$ or $|0\rangle$, produce a superposition $\alpha|0\rangle + \beta|1\rangle$. Any algorithm can, in principle, be realized as a sequence of such unitary rotations and universal quantum gates, operating on two coupled qubits.[1]
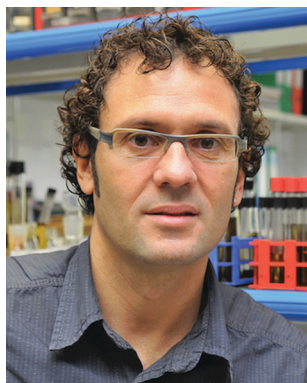
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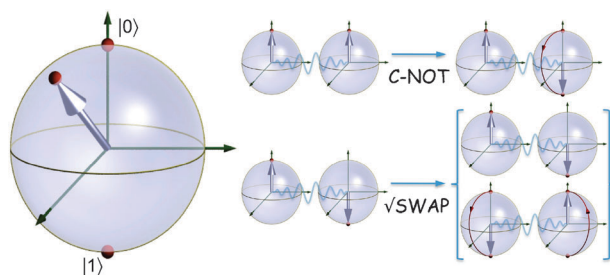
Fig. 1 Left, schematic representation of a qubit: the points on the Bloch sphere represent the permitted states of the qubit two-dimensional space $\alpha|0\rangle + \beta|1\rangle$, where α and β are complex numbers with $|\alpha|^2 + |\beta|^2 = 1$. Right, representation of CNOT and $\sqrt{\text{SWAP}}$ operations; only the $|1,1\rangle \rightarrow |1,0\rangle$ (for the CNOT) and $|1,0\rangle \rightarrow (|1,0\rangle + i|0,1\rangle)/(1 + i)$ (for the $\sqrt{\text{SWAP}}$) transformations are shown.

Archetypes of such universal QGs are the *controlled-NOT* (CNOT) and the $\sqrt{\text{SWAP}}$ (Fig. 1, right) gates. The CNOT gate inverts the state of one qubit (*target qubit*) if and only if the other (*control qubit*) is in the $|1\rangle$ state. The $\sqrt{\text{SWAP}}$ turns a two-qubit state $|a,b\rangle$ (with a and b being 0 or 1, and different) into a superposition $(|a,b\rangle + i|b,a\rangle)/(1 + i)$.[5,6] Both the CNOT and the $\sqrt{\text{SWAP}}$ gates return a 2-qubit output that might correspond to an *entangled* state, *i.e.* a state that cannot be expressed as a product of states of each of the two quantum systems embodying the QG. In the case of the CNOT gate, entanglement occurs when the input control qubit lies in a superposition of two states. Entanglement is a natural occurrence of quantum systems that are correlated by some weak interaction.[7] In order to achieve the implementation of some QC algorithms, it is necessary that the possibility exists of generating entanglement between the states of two connected qubits.

Currently, the potential of QC for the realization of algorithms to solve efficiently extremely complex problems has been well established at the theoretical level.[1–4] However, the physical implementation of quantum information processing (QIP) is an extremely challenging task and remains far from being a reality. One could argue that QC may be the inevitable consequence of the miniaturization of electronic devices: with components' size reaching the nanoscale, quantum mechanics laws are expected to take over, and thus provide the ingredients for the realization of QIP.[1,8–10] A number of potential candidates have been proposed and investigated as the physical systems to constitute the hardware of QC.[8] The range of proposed systems spans a wide spectrum of modern materials physics and includes ion traps,[11] photons,[12] nuclear spins,[13] superconducting circuits[14] or spin-based systems such as electrons confined to quantum dots in semiconductors.[10,15]

Among the most attractive candidates to become the qubits of future quantum computers are electronic spins. As isolated species, they constitute true two-level systems, while any radical or open-shell metal-containing molecule may be appropriate carriers of such qubits.[16,17] The realization of algorithms requires the organization of qubits into QGs capable of undergoing logic operations with these qubits. Quantum computation could be carried out if an appropriate and addressable set of quantum gates are disposed in a scalable manner.[18] Coordination magnetic molecules could

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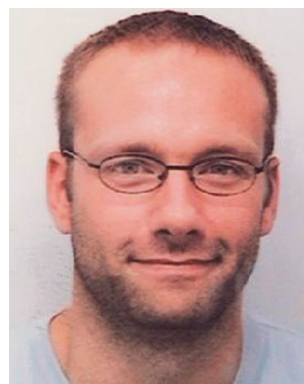
Olivier Roubeau graduated in Inorganic Chemistry at Versailles-Saint-Quentin-en-Yvelines and Paris VI Universities (1998), working with Prof. G. Férey at Institut Lavoisier Versailles, and then obtained his PhD from Leiden University (2002) with Prof. J. Reedijk. He was then assistant professor in Physical Chemistry at University of Bordeaux and CNRS-CRPP until 2008, when he became permanent researcher of the Spanish CSIC at ICMA in Zaragoza, where he focuses on synthesis and physical studies of functional magnetic coordination complexes, and their organization onto surfaces or into soft matter phases.

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serve for the construction of 2-qubit QGs, offering important advantages over other proposed systems; all molecules are identical, their structure may be easily tuned through chemical methods and their behaviour is governed purely by quantum mechanics.[19,20] It is not strictly necessary that the qubits of such QGs consist of monoelectronic $S = 1/2$ systems. The two state levels may be embodied by any spin system that in a certain regime exhibits two states (*effective* $S = 1/2$) such as the isolated ground state of a collection of antiferromagnetically exchanged coupled spin moments S_i,[21,22] or the two level system of the ground state of highly anisotropic lanthanides.[23] Coordination chemistry provides means of assembling *within a molecule* two such paramagnetic ions or groups of strongly-coupled open-shell metals, while interconnecting them through convenient and potentially switchable interactions. The use of specifically designed or selected multidentate ligands is at the core of this rational synthetic approach to QC. This *tutorial review* aims at defining the requirements of such coordination assemblies for their use in QC, briefly reviews the few existing proposals, and develops in more detail our initial approaches to the preparation of such smart materials.

2 Requirements for spin-based molecular quantum gates

The basic conditions that any physical system needs to fulfil in order to act as a QG were clearly defined by Di Vincenzo a decade ago in the form of five criteria (plus two more to implement quantum communication).[9] These remain valid for potential spin-based QGs, as discussed in more detail elsewhere.[10,17] Here, we shall discuss them in relation to the endeavour of designing the synthesis of coordination molecules as candidates for 2-qubit QGs. Along this idea, these requirements can be summarized and expressed as follows:

(i) Properly defined and scalable qubits

In molecular spin-systems, this means that each spin qubit is sufficiently isolated within the molecule to exhibit a proper two-level qubit basis $|1\rangle$ and $|0\rangle$ (which will be denoted as $|\Uparrow\rangle$ and $|\Downarrow\rangle$ from now on), well separated from any possible excited states. This is the case of a true spin 1/2 moiety such as a Cu(II) ion isolated within a complex molecule, but also in principle for any metallic aggregate having, under certain conditions, a well-isolated ground-state doublet. This may also be the case for lanthanide ions within a strong crystal field or metal cluster complexes of particular characteristics (see below).[21–23] Scalability is a key factor to build realistic quantum computers. It implies the possibility of engaging many identical qubits, while still adhering to all requirements presented here. This is also important for quantum error correction, for which some mechanisms have been proposed that require additional qubits.[9] Chemical methods are particularly attractive in this respect since macroscopic arrays of identical molecules are naturally accessible. The actual disposition of truly identical molecules within a device (typically on its surface) is nevertheless not as straightforward. The misalignment or molecular isomerism induced through the interaction with the surface may easily result in codification

information errors. In this respect, the use of robust complexes containing one or several qubits as defined above, externally functionalized for grafting them to a surface while keeping the chemical structure, appears as a good avenue. It has also been proposed that Single-Molecule Magnets (SMMs) could serve to implement quantum computation, through the multiple M_S states accessible within their high-spin ground state.[24] Nevertheless, relying on single multilevel systems impedes true scalability.[10] Therefore such proposals do not seem appropriate under this criterion.

(ii) Easy and efficient initialization

One should be able to set each qubit in a well-defined initial state at any time and in an efficient manner. For a molecular spin, this can simply be done by taking it into its grounds state, *e.g.* by cooling it under a magnetic field. Quantum error correction, which is inherent to real world quantum operations, requires the supply of additional "fresh" qubits.[8,9]

(iii) Long decoherence times

The decoherence time (τ_d) characterizes the quantum dynamics of a qubit in contact with its environment.[25] It is the time during which the quantum information stored in a qubit is maintained before it is lost because of the interaction with the surroundings. For QC operations it is of course fundamental that the quantum nature of the qubits is tenable. Originally, this was thought to be a major obstacle for electronic spins to be considered as potential qubits. It is generally accepted that the decoherence times should be at least 10^4 times larger than the time required for the basic computation action, the so-called gate time (τ_{gate}, see below). This is a stringent condition, especially considering that the value already takes into account the implementation of quantum error corrections, which allows a reduction of the decoherence time.[9,26] Limiting decoherence must therefore be one of the main factors to take into account in the chemical design of QGs. Pulsed EPR has been the primary tool for investigating and characterizing the coherent spin dynamics of molecular spin systems.[22,27–30] For spin-based qubits, decoherence can mainly arise through interaction with phonons and nuclear spins, as well as dipolar interactions with neighbouring qubits. In this respect, the necessary coupling between qubits during computation may be in itself a source of decoherence. Dipolar interactions can in principle be reduced by using low-spin systems and controlling the disposition (topology/distance) of the qubits. Studies on diluted solutions of [Cr$_7$Ni] (see below)[29] qubits showed for the first time the feasibility of performing coherent manipulations of their $S = 1/2$ molecular spins. These experiments also revealed that the hyperfine coupling between the electronic and the nuclear spins is the main source of decoherence (with estimated τ_d of a few μs). More recently, the quantum Rabi oscillations observed on frozen solutions of [V$_{15}$] clusters (a polyoxometallate anion with a formula [V$_{15}$As$_6$O$_{42}$(H$_2$O)]$^{6-}$) separated by cationic surfactant molecules were studied and their frequency measured.[22] Here also, the decoherence, characterized by relaxation times τ_d of the order of 800 ns, was mainly attributed to the hyperfine coupling with the ^{51}V nuclear spins. In this respect, metals exhibiting a nuclear spin could be problematic if these

cannot be enriched with a zero-spin isotope. Nitrogen donor ligands may also pose difficulties, since these locate spin active nuclei (^{14}N; $I = 1$) very close to the electronic spins. The amount of hydrogen nuclei should also be limited as much as possible, although their location further away from the unpaired electrons may cause little decoherence.[22,29]

(iv) Implementing universal quantum gates

Molecules containing two well defined qubits fulfilling the above conditions and the properties described in what follows might provide attractive prototypes for the universal CNOT and $\sqrt{\text{SWAP}}$ quantum gates. For the realization of a CNOT, both qubits must exhibit a mutual interaction much smaller than the energy difference between both states within each qubit in the presence of an external magnetic field, which may be achieved with strong axially anisotropic spins. In addition, the control and target qubits must be different so they can be addressed specifically. Therefore, the structure of the molecule should impose this dissymmetry between both qubits. The $\sqrt{\text{SWAP}}$ gate on the other hand requires that the spins of both qubits exhibit a weak antiferromagnetic Heisenberg-type coupling that one must be able to modify at will during a desired period of time (gate time), in order to let the system evolve quantum mechanically so as to undergo the transformation dictated by this operation.[31] In order to carry out these two operations it is necessary that the qubits of the QG have the possibility to exhibit entangled states. Aspects of entanglement in spin-based systems have been discussed in detail recently, showing in particular that the magnetic susceptibility may be used as a so-called entanglement witness.[17,32]

(v) Readout of qubits

The state of the target qubits within the quantum gates, *i.e.* the output, has to be determined once the computation is finished. This implies that any qubit, including those within QGs, has to be addressed selectively, either spatially, spectrally, magnetically or by any other means.

It is clear from above that implementing QC using coordination chemistry is a very difficult prospect, and a huge synthetic challenge. Work in this direction seems limited to only few groups devoted to chemical synthesis and it has only started to surface. The following sections summarize some of the most important reported examples of molecular systems portrayed as prototypes of spin-based QGs that have arisen from coordination chemistry, as well as some of the work carried out in our laboratory in order to face this challenge.

3 Current coordination chemistry proposals of 2-qubits

Despite the many advantages that electronic spins of discrete molecules may offer as the possible hardware in QIP, very few coordination systems have been proposed for this purpose. A reason for this is presumably that the awareness of this potential is only beginning to grow among coordination chemists and therefore the full reach of their synthetic skills has not yet been put to its service. In addition, the conditions that molecules must fulfill to realize universal quantum gates,

i.e. the magnetic asymmetry in the case of CNOT gates and the switchability of magnetic interactions needed for $\sqrt{\text{SWAP}}$ operations, are difficult to achieve. We review in this section the few systems that have been explicitly portrayed as models of 2-qubit QGs and also a few examples in the literature that exhibit interesting properties in this respect, even if they have not been studied in such context.

Currently, one of the most versatile approaches to QIP using molecular chemistry is linking heterometallic rings of transition metals to either covalent or supramolecular assemblies of two such units. The original family of these rings is very extensive and they exhibit the general formula $(NH_2R_2)[Cr_7MF_8(O_2CR')_8]$ (M^{II} = Mn, Fe, Co, Ni, Cd; R, R' = various).[33] Among these, the Ni derivative is suitable as a possible qubit, since it exhibits a spin ground state $S = 1/2$, well separated energetically from excited states. One feature of these molecular rings that is attractive for QC is that they exhibit relatively long spin decoherence times. This has been determined by measuring through pulsed EPR spectroscopy the dephasing time, T_2, which at 4 K amounts to 0.4 μs, enabling the realization of coherent quantum operations within a molecule.[29]

Controlling the magnetic interaction between two connected rings is also essential for their role as 2-qubit QGs. The linking of the rings has been achieved in three different ways:[35] (i) exploiting a combination of coulombic and H-bonding interactions between the (anionic) rings and diammonium long linkers, (ii) selectively replacing a carboxylate from the ring by another one acting as the linker, and (iii) using ring derivatives that contain one labile coordination site through which two of them can be linked. The first strategy has produced systems with and without the presence of additional paramagnetic elements (Cu^{II}) in between the rings, depending on the nature of the linker.[36] It has usually led to spectacular architectures exhibiting however negligible magnetic coupling between their various parts. The second method allows the inclusion of carboxylates that can coordinate to a free Cu(II) ion, the latter acting as a "glue" between two rings, also mediating the magnetic interaction between them (Fig. 2). This interaction is shut off if instead of a single ion the
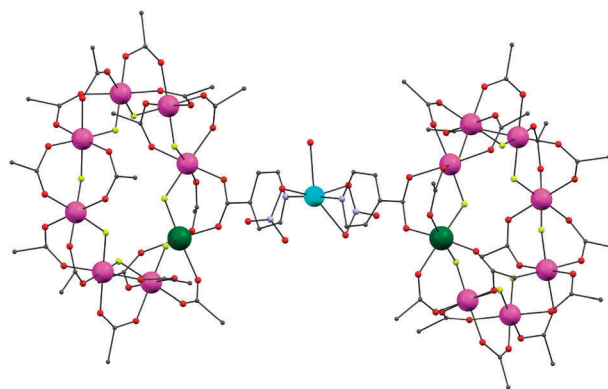

Fig. 2 Representation of the anion of a "double-ring" assembly involving a paramagnetic bridge (Cu^{II}), with a formula ([NH$_2$Pr$_2$]-[Cr$_7$NiF$_8$(O$_2$CCMe$_3$)$_{15}$(O$_2$CC$_5$H$_4$N)])$_2$[Cu(NO$_3$)$_2$(OH$_2$)].[34] Dark green, Ni; pink, Cr; turquoise, Cu; yellow, F; red, O; purple, N; rest, C. H atoms excluded.

bridging element is a pair of strongly antiferromagnetic Cu(II) ions.[34] The last approach is attractive because it allows the use of a large variety of bidentate bridging ligands to connect two wheels, providing a way of finely tuning the magnetic exchange between both parts of the assembly.[37]

The demonstration that pairs of single molecule magnets (SMMs) exhibit quantum superpositions of their spin wave functions is of great significance in this context, since such entanglement is the necessary ingredient for the realization of QC operations by multi-qubit QGs. SMMs are high spin clusters that exhibit slow relaxation of their molecular magnetic moment.[38] Therefore, each of these molecules behaves as a tiny magnet. The superposition of the spin ground states of a pair of SMMs with a formula $[Mn_4O_3Cl_4(O_2CEt)_3(py)_3]$, held together in the crystal lattice by means of supramolecular interactions, was shown through high field EPR.[39] The literature contains other discrete coordination clusters that could be very interesting in this context. One relevant example is a family of helicate clusters with formulae $[(CuLn)_2L_2(NO_3)_6-(H_2O)_2]$ (Ln^{III} = Gd, Y, Tb; H_2L = a bis-iminophenol flexible ligand), featuring in the same molecule two weakly coupled heterometallic dinuclear entities (Fig. 3).[40] The CuTb derivative is particularly important since it exhibits slow relaxation of the magnetization, which can only be attributed to the properties of each of the two dinuclear entities of the molecule. This unusual fact was not emphasized when these compounds were reported. Only the observation of intramolecular based exchange bias of the magnetization (perhaps for the first time!) is briefly mentioned.

Another relevant molecular system, which constitutes the theoretical basis for an interesting proposal to realize $\sqrt{SWAP}$ quantum gate operations, is a polyoxometalate with a formula $[PMo_{12}O_{40}(VO)_2]^{q-}$.[41] This compound consists of a mixed valence Keggin cage of Mo(V/VI), capped at both ends by two $(VO)^+$ units, each with a spin moment of $S = 1/2$. The core of the cage acts as a reservoir of a variable number of electrons delocalized over the Mo ions. If the number of the core electrons is even, the resulting central spin is zero and the $(VO)^+$ units are then weakly coupled antiferromagnetically. If instead, the core hosts an odd number of electrons, its spin is $S = 1/2$, the ensemble thus featuring a total of three coupled $S = 1/2$ spins. A very appealing aspect of this system is that it could be addressed by electrical means so that electrons may be injected or extracted at will, which would allow to control the interaction between the $S = 1/2$ moments of the $(VO)^+$ groups by switching on and off the presence of the central spin.
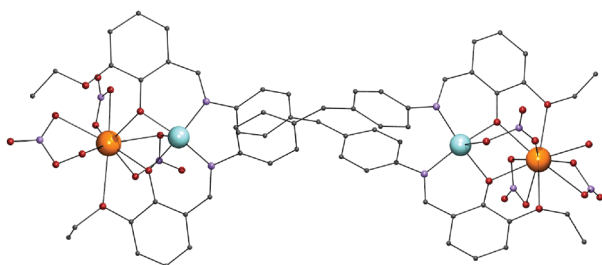
This would allow the realization of a $\sqrt{SWAP}$ operation if the central spin is maintained during a given amount of time (gate time, τ_{gate}), which must fulfil a certain relation with the intramolecular magnetic exchange constants.[6]
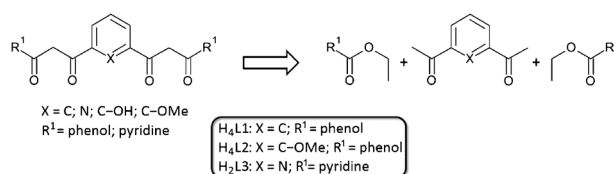
An interesting development in the realization of spin-based qubits for QC is the demonstration that different transition metal centers in molecular helicates may also show different gyromagnetic factors, that is, a different Zeeman interaction with an external magnetic field. This property might enable addressing them specifically by use of pulsed Q-band EPR. This was chemically engineered in a dinuclear triple stranded helicate of Mn(II), using a four-membered oligo-imidazole ligand.[42] In fact, there are many metallic helicates of this kind in the literature. This work underscores the benefits of a good dialog between chemists, physicists and engineers for the advance of applied nanosciences.

In the following sections we review the results obtained from the design and use of a series of β-diketone based ligands for the preparation of coordination molecular assemblies as potential prototypes for 2-qubit QGs.

4 Design of multidentate ligands to access 2-qubits

Our synthetic approach towards the preparation of potential qubit systems involves the engagement of the β-diketone coordinating unit. This O-donor chelating ligand has proven its value in the creation of remarkable metallocluster assemblies.[43] The synthesis of β-diketonic molecules is usually straightforward. Multidentate ligands can easily be obtained through a simple Claisen condensation, sketched in Fig. 4.[43]

The first category of targeted qubits, *i.e.* molecular pairs of well-defined, weakly coupled metal clusters, is achieved using poly β-diketone ligands exhibiting two groups of "coordination pockets" (Fig. 4). These pockets serve to aggregate metals in close proximity (as in molecules of "*class A*"; defined below) or simply to clamp pre-formed clusters and link them to each other ("*class B*" molecules; see below). These ligands are obtained by condensation of two ketone molecules with a diester (usually ethyl esters), in the presence of a base (for instance, sodium hydride). Hence, a large variety of multidentate ligands can be prepared through a simple and highly versatile synthetic route. If additional donor groups are featured on the position "X", the ligands may then act as a "template" for the aggregation of metals into linear clusters which can then be linked as molecular pairs by auxiliary ligands ("*class C*" molecules, see below). Thus, ligands such as H_4L1, H_4L2 and H_2L3 (see Fig. 4) have in this manner been designed in our group, and some of their coordination compounds are described in the following section (Molecules featuring two weakly coupled clusters).

Fig. 3 Representation of $[(CuLn)_2L_2(NO_3)_6(H_2O)_2]$ (Ln^{III} = Gd, Y, Tb). Colors as in Fig. 2, plus orange, Ln. H atoms excluded.[40]

X = C; N; C–OH; C–OMe
R^1= phenol; pyridine

H_4L1: X = C; R^1 = phenol
H_4L2: X = C–OMe; R^1 = phenol
H_2L3: X = N; R^1= pyridine

**Fig. 4** Synthetic pathway for the preparation of poly β-diketonic ligands through Claisen condensation.[43]
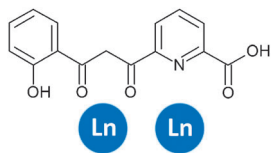
Fig. 5 Schematic representation of the ligand H_3L4, aimed at coordinating two lanthanide ions (Ln).

Eventually, such ligands might be modified so as to engineer a structural dissymmetry within the cluster.

The second category of qubits that we aim to synthesize, namely the dinuclear complexes of anisotropic metal ions, is achievable with β-diketonic ligands such as H_3L4, which is depicted in Fig. 5. H_3L4 is an asymmetric β-diketone exhibiting additional functional groups, namely a phenol unit and a pyridine-2-carboxylic acid moiety. Hence, the coordination of two highly anisotropic metal ions, as could be the lanthanides (Ln), may generate dinuclear complexes whose metal centres could display distinct environments; therefore, two inequivalent qubits may be integrated within the same molecule. If the interaction between these is weak, they might constitute a model for a CNOT QG (see section Complexes of two dissimilar and weakly coupled lanthanides).

5 Molecules featuring two weakly coupled clusters

The first proposals for using molecular nanomagnets (or SMMs) to implement the qubits for QC[24] naturally give place to the idea that molecules featuring two well-defined coordination clusters could represent ideal systems for realizing 2-qubit QGs, if these clusters exhibit the appropriate spin properties. In this section, we describe the progress made towards the synthesis of such molecular architectures using bis-β-diketone ligands. In exploring this chemistry, we identified a series of molecular assemblies responding to this definition, which could be divided into three classes depending on the structural role played by the multidonor β-diketone, L, within them. These assemblies are schematically represented in Fig. 6 and are defined next. In "*class A*" molecules, L is responsible for having metals grouped into two clusters and also keeping both aggregates together within the molecule. In molecules of "*class B*", the metal clusters are held together by other ligands while L links them pairwise within molecules. Finally, in the case of molecules of "*class C*", L gathers metals as clusters that are then linked as pairs by external ligands. Examples of each class are described below, together with discussions with regard to their potential as 2-qubit QGs.
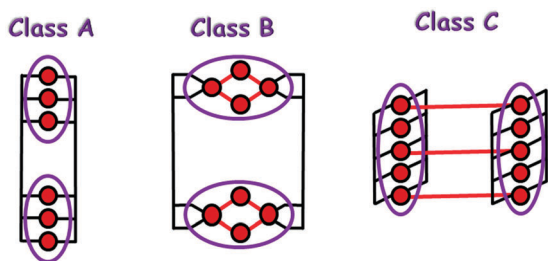

Fig. 6 Schematic representation of *classes A*, *B* and *C* molecular cluster pairs as defined in the text. Black and red lines represent multidonor β-diketone (L) and additional auxiliary ligands, respectively.

5.1 *Class A* cluster pairs

Ligand H_4L1 is ideal for the construction of this type of clusters, given the alignment of its coordination pockets as two separate groups. Reactions of H_4L1 with divalent transition metals in coordinating solvents using strong basic conditions produce assemblies that can be described as two dimetallic entities well separated within one molecule. In Fig. 7 are represented the Cu^{II} and Ni^{II} analogues, $[Cu_4(L1)_2(py)_4]$ and $[Ni_4(L1)_2(py)_6]$, made in pyridine. The corresponding complex with Co^{II} has also been prepared.[44]

In all these compounds, the deprotonated species $L1^{4-}$ organizes the metals as molecular linear arrays by saturating all their equatorial coordination sites, while solvent molecules occupy some axial sites. It is interesting to note that, while all the Cu^{II} ions exhibit their preferred square-pyramidal pentacoordinated geometry, in $[Ni_4(L1)_2(py)_6]$, the inside Ni^{II} ions are six-coordinate (as usual) whereas the external metals are five-coordinate (much more uncommon). The latter situation is also observed in the Co^{II} derivative. This is related to structural constrains to achieve six coordination as imposed by the whole architecture and it could be exploited to prepare heterometallic assemblies with selective disposition of different metals within the molecule (see below).

These systems appear topologically appropriate as 2-qubit assemblies. However, bulk magnetic measurements indicate that the metals within each dinuclear fragment always couple antiferromagnetically, therefore, the ground state spin of each fragment vanishes. A possible way to have suitable qubits on each side of the molecule is by locating metals with different spin numbers within each of the pairs. The preferences in coordination geometry observed for the various positions of the tetranuclear assemblies (see above) suggest the possibility of achieving this by making heterometallic complexes. This could be done by mixing in the reaction a metal with preference for five coordination (Cu^{II}; $S = 1/2$) together with a metal prone to adopt the octahedral geometry (Ni^{II}; $S = 1$). In Fig. 8 is the structure of the heterometallic cluster $[Cu_2Ni_2(L1)_2(py)_6]$, obtained in this manner.[44] Good evidence
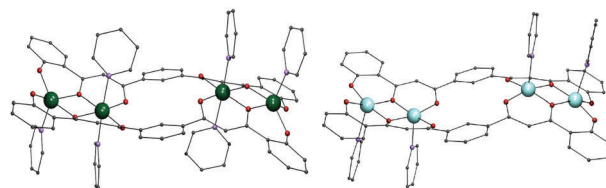
Fig. 7 Representation of $[Cu_4(L1)_2(py)_4]$ and $[Ni_4(L1)_2(py)_6]$. Colors as in Fig. 2. H atoms excluded.
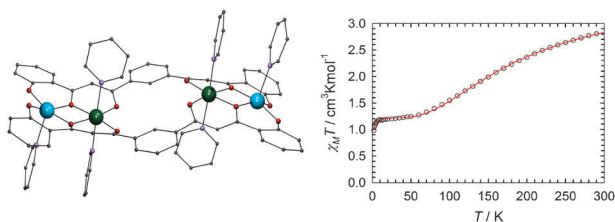
Fig. 8 Representation of $[Cu_2Ni_2(L1)_2(py)_6]$ (left). Colors as in Fig. 6 (H atoms excluded) and its $\chi_M T$ *vs.* T curve (right). The red line is a fit of the experimental data (see the text).

of the topology as revealed from X-ray single crystal diffraction came from metal analysis, which confirmed the 1 : 1 ratio of both metals in the bulk of the sample. Additionally, the molecular structure of the compound, which is considered representative of the bulk (since the sample is homogeneous), was calculated by DFT methods to have much higher energy for any distribution of two Ni^{II} and two Cu^{II} ions other than the $CuNi\cdots NiCu$ sequence suggested by the refinement of the crystallographic data (Fig. 8, left).

Confirmation that each Ni^{II} ion in this compound is coupled antiferromagnetically to a Cu^{II} comes from bulk magnetization data (Fig. 8, right), the fit of which gave $J_{Ni-Cu} = -72.9$ cm^{-1} (in the $H = -2JS_1S_2$ convention). Both [CuNi] pairs of the cluster exhibit $S = 1/2$ ground states, that are weakly coupled, as necessary for a 2-qubit QG. From its physical behavior, this molecule may be considered equivalent to many of the ring pairs discussed previously. The potential of entanglement of the spin wave functions of both qubits needs to be studied in detail. Also, the synthesis may be refined in order to ensure that both sides of the molecule are non-equivalent.

5.2 Class B cluster pairs

The strategy for preparing this type of architecture is to create conditions for the formation of transition metal clusters in the presence of a ligand L, suitable to link them as separate entities within one molecule. It is known from the literature that Mn^{III} trinuclear aggregates of the type $[Mn_3O(O_2CR)_6(S)_3]X$ (R = various; S = solvent ligands; X$^-$ = various anions, Fig. 9, left) rearrange in the presence of some β-diketones forming tetranuclear aggregates, usually called "butterfly", featuring the chelate as terminal ligands at both ends (Fig. 9, right).[45] The use of a bis-β-diketone could lead to molecular pairs of such aggregates. H$_4$L2 seems appropriate for this purpose since it displays two 1,3-dicarbonyl units separated by a methoxyphenylene moiety, which prevents the formation of class A assemblies, simply for steric reasons.

Indeed, the reaction of H$_4$L2 with $[Mn_3O(O_2CR)_6(py)_3]$-(ClO$_4$) (R = Me, Ph, pMePh; py = pyridine) leads to the corresponding assemblies $[Mn_8O_4(O_2CR)_{12}(H_2L2)_2(pz)_2]$ if the additional bridge pyrazine (pz) is present.[46] These remarkable clusters feature two well-defined "butterfly" moieties, weakly connected within a stable molecule (Fig. 10). The robustness of these assemblies is confirmed by ^{1}H NMR, which shows unambiguously that their structure is maintained in solution of chloroform.
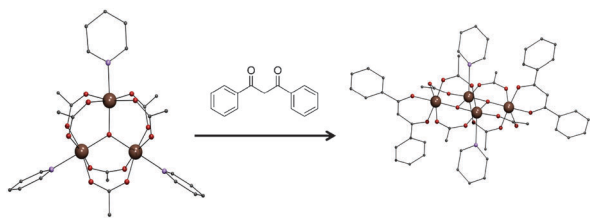
Fig. 9 Representation of the cation $[Mn_3O(AcO)_6(py)_3]^+$ and $[Mn_4O_2(AcO)_6(dbm)_2(py)_2]$, obtained from the reaction of the former with dibenzoylmethane (Hdbm).[45] Colors as in Fig. 2, plus dark brown, Mn. H atoms excluded.
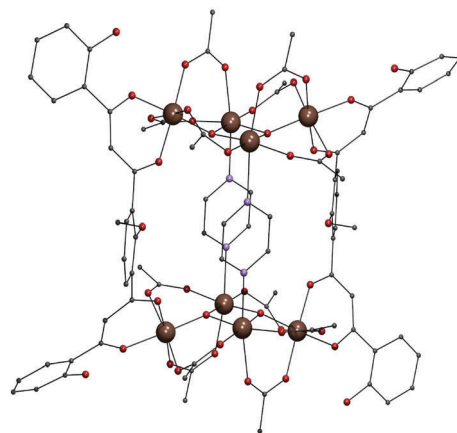
Fig. 10 Representation of the molecular cluster pair $[Mn_8O_4(AcO)_{12}$-(H$_2$L2)$_2$(pz)$_2$]. Colors as in Fig. 9. H atoms excluded.

Variable temperature bulk magnetization measurements under a constant magnetic field show that a combination of ferro- and antiferromagnetic interactions within the tetranuclear moieties leads to a lowest energy spin state of $S = 2$ for each [Mn$_4$] fragment. If these two half-molecules were isolated, their spin state immediately above would be ~ 10 cm^{-1} higher in energy. Instead, both sides exhibit a weak antiferromagnetic interaction of nearly -1 cm^{-1}. For this molecule to constitute a 2-qubit QG, both tetranuclear moieties should exhibit *effective* $S = 1/2$ spin moments at the ground state. This could be the case at very low temperature if the spin ground state of these fragments were of the Ising type. Ultra-low temperature measurements should help to elucidate this question.

This reactivity is not exclusive to manganese; the reaction of the Fe^{III} cluster $[Fe_3O(OBz)_6(py)_3](NO_3)$ (HOBz = benzoic acid) with H$_4$L2 and pyrazine produces the analogous cluster pair $[Fe_8O_4(BzO)_{12}(H_2L2)_2(pz)_2]$. In this case, the same procedure in the absence of pyrazine allows the preparation of another cluster of the same category, $[Fe_6O_2(BzO)_{10}(H_2L)_2$-(py)$_2$], consisting of a pair of triangles linked within the same molecule by H$_2$L2^{2-} units.[47] The magnetic properties of the latter reveal that the assembly is composed of two $S = 5/2$ moieties (resulting from antiferromagnetic interactions within each approximately isosceles triangle). Each of these units may act as a qubit if the transitions between the $M_S = +1/2$ and $M_S = -1/2$ of the $S = 5/2$ sextets are addressed selectively.[42] The magnetic study also shows that the triangles exhibit weak antiferromagnetic coupling. Assemblies of this kind could constitute $\sqrt{\text{SWAP}}$ QGs if the bridging bis-β-diketone is modified at the central position to incorporate an electroactive or photoactive component that could serve to turn on and off the interaction between both qubits during the appropriate gate times (τ_{gate}).

There are some other compounds in the literature that respond to this definition of molecular cluster pairs that would be worth studying under this perspective.[48,49]

5.3 Class C cluster pairs

Systems under this category consist of closely spaced metals grouped by ligands designed to do so, which are then linked to molecular pairs by other external ligands. A way of doing this
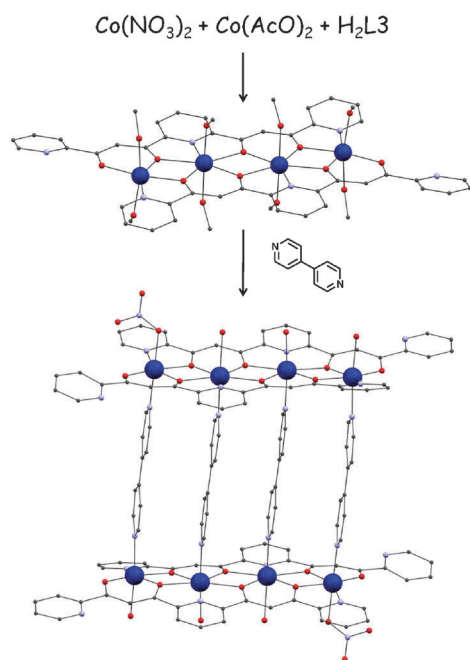
Fig. 11 Representation of the cation of $[Co_4(L3)_2(MeOH)_8](NO_3)_4$ and the reaction leading to it (top) and the molecular structure of the cation of $[Co_8(L3)_4(OH)_2(H_2O)_4(NO_3)_2(bpy)_4](NO_3)_4$ (bottom). Colors as in Fig. 2, plus blue, Co. H atoms excluded.

using bis-β-diketones is well represented by the chemistry of ligand H_2L3 with Co^{II}. It was first demonstrated that this multidonor has the ability to stabilize linear metal chains such as the cluster $[Co_4(L3)_2(MeOH)_8](NO_3)_4$ (Fig. 11).[50] This complex features four aligned Co^{II} ions sandwiched by two $L3^{2-}$ donors that occupy all their equatorial sites, forming a very flat platform. Each metal also has its two axial coordination sites occupied by molecules of methanol, leading to distorted octahedral (outer ions) and pentagonal bipyramidal (central metals) coordination geometries. These axial positions are highly labile, as demonstrated by the fact that they can be replaced completely by water molecules from atmospheric moisture. This suggests the possibility of using these coordination sites as a way of linking the $[Co_4]$ clusters to each other. Indeed, the use of a difunctional ligand such as 4,4′-bipyridine (bpy) in the above reaction allows the formation of the cluster pair $[Co_8(L3)_4(OH)_2(H_2O)_4(NO_3)_2(bpy)_4](NO_3)_4$ (Fig. 11).[51]

The main drawback of this assembly as a possible 2-qubit QG is the fact that each cluster within the molecule has an $S = 0$ ground state as a result of antiferromagnetic exchange coupling between the metals. One way of solving this problem would be to variate the oxidation state of some metals of each chain electrochemically.

6   Complexes of two dissimilar and weakly coupled lanthanides: molecular prototypes of CNOT QGs

One possible way of having two inequivalent qubits within a molecule, as required for a CNOT QG, is using non-symmetric ligands. Ligand H_3L4 exhibits a collection of donor groups disposed in a way that could favour the aggregation of two metals in different coordination environments. This is the case

with lanthanide, Ln^{III}, cations. Indeed, single lanthanide ions are good candidates for encoding quantum information, since they very often exhibit, as a result of their strong zero field splitting (ZFS), a very well isolated ground state doublet, $\pm m_J$, which represents an *effective $S = 1/2$*, thus providing for good realizations of qubits. In addition, their spin states exhibit long decoherence (with measured relaxation times, T_2, of up to 7 µs), adding a very important quality to their functionality in QC.[22] The reaction of H_3L4 with LnX_3 (Ln^{III} = a lanthanide; X^- = Cl^- or NO_3^-) in pyridine forms dinuclear complexes with a general formula $[Ln_2X(HL4)_2(H_2L4)(py)(S)]$ (S = py or H_2O) for practically the entire *4f* series.[52] All these compounds involve two Ln^{III} ions surrounded by three deprotonated H_3L4 ligands along the molecular axis, thus, with one side of the complex being different from the other. In Fig. 12 is a representation of the compound $[Tb_2Cl(HL4)_2(H_2L4)(py)_2]$, emphasizing the difference between the coordination environments of both metal ions. On the right side of Fig. 12 are $\chi_M T$ *vs.* T plots for the $[Tb_2]$, $[Gd_2]$ and $[Eu_2]$ analogues. At high temperatures, the curve of the gadolinium complex denotes a Curie-like behavior corresponding to a couple of independent Gd(III) ions ($S = 7/2$) down to near 10 K, where a small decline is observed reflecting a very weak antiferromagnetic coupling between both cations. The red solid line in this curve is a fit of the experimental data that reveals the coupling constant to be $J = -0.014$ cm^{-1} (in the $H = -2JS_1S_2$ convention). A very weak coupling between both qubits is necessary for the realization of a CNOT quantum gate, together with a strong anisotropy of both spin carriers. The curve of the europium complex shows that the ground state of each metal is diamagnetic ($J = 0$), with some paramagnetic Stark levels populated at higher temperatures. The case of terbium is the most relevant for QC; the high temperature $\chi_M T$ values are consistent with two uncoupled Tb^{III} ions ($^7F_6$, $S = 3$, $L = 3$, $J = 6$, $g = 3/2$) whereas the decline observed upon cooling is a consequence of the depopulation of the various m_J states, down to the Ising limit where only the two orientations $m_J = \pm 6$ of the $J = 6$ state of each metal are populated. These orientations correspond to the two states embodying each qubit. Ac magnetic susceptibility and heat capacity studies performed on this complex in a very broad temperature range (from room temperature down to 100 mK)
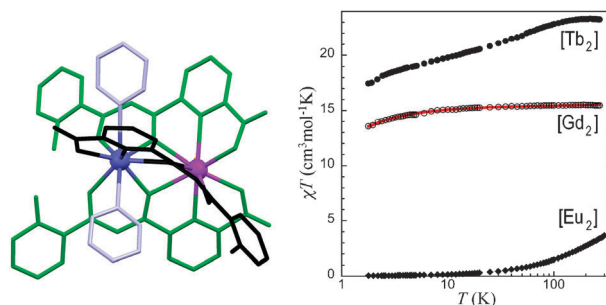
Fig. 12 (left) Representation of $[Tb_2Cl(HL4)_2(H_2L4)(py)_2]$ emphasizing the inequivalence of both metal sites. Deprotonated H_3L4 ligands are in black and green, py is in light blue. H atoms excluded. (right) $\chi_M T$ *vs.* T plots for the $[Tb_2]$, $[Gd_2]$ and $[Eu_2]$ analogues. The red line is a fit to the experimental data (see the text).
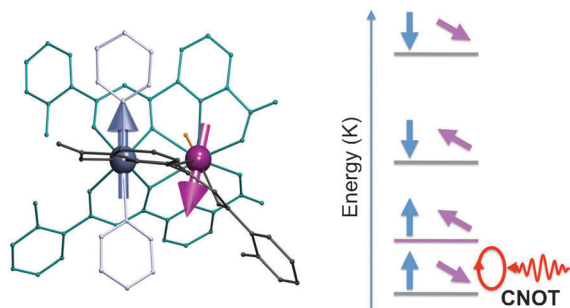
Fig. 13 (left) Dissimilar coordination environments of Tb(III) ions in complex [Tb$_2$Cl(HL4)$_2$(H$_2$L4)(py)$_2$], emphasizing the two different orientations of their anisotropy axes. (Right) Energy diagram of the [Tb$_2$] complex under a magnetic field H, representing the four states, $|1,1\rangle$, $|1,0\rangle$, $|0,1\rangle$ and $|0,0\rangle$, of a CNOT QG and the realization of this operation.

enabled us to determine the axial ZFS parameter D ($D = 12$ cm^{-1}, using the Hamiltonian $H = -D[J_{1,z}^2 + J_{2,z}^2]$ and the appropriate temperature regime) of the metals and also the magnetic exchange, J_{ex}, between them ($J_{ex} = -0.011$ cm^{-1}, in the $H = -2JS_1S_2$ convention). This, together with the evidence that these two ions are not equivalent, is a demonstration that the [Tb$_2$] molecule provides a good realization of two coupled and magnetically distinguishable qubits.[53] The magnetic inequivalence between both metals is manifested by the observation that cooling down to very low temperature does not cause the product $\chi_M T$ to vanish. This is because the anisotropy axes of the metals in each molecule form an angle δ different than zero, causing the two antiferromagnetic states $|\Uparrow\rangle_1 \otimes |\Downarrow\rangle_2$ and $|\Downarrow\rangle_1 \otimes |\Uparrow\rangle_2$ to preserve a net magnetic moment (Fig. 13, left). The low temperature susceptibility and heat capacity measurements furnish, independently, an estimation of the angle δ of 66°. This is confirmed by isothermal magnetization measurements (at $T = 0.26$ and 2 K) which show that the antiferromagnetic states give a paramagnetic response starting at $H = 0$, contrary to what would be observed if the magnetic moments of both metals cancelled each other. The angle formed between both anisotropy axes makes the magnetic moment of each metal to couple differently to an external magnetic field, H, applied in a given orientation, thus making both spins inequivalent. The energy level structure of the [Tb$_2$] complex (Fig. 13, right) fulfills then all the ingredients of a CNOT QG. Indeed, the magnetic asymmetry allows to single out any of the desired transitions necessary for the realization of a CNOT operation. For example, at $\mu_0 H = 0.28$ T, only the two states that could convert into each other during such operation (i.e. those with the control qubit up; $|\Uparrow\rangle_1 \otimes |\Downarrow\rangle_2$ and $|\Uparrow\rangle_1 \otimes |\Uparrow\rangle_2$) are separated by the energy of 9.8 GHz radiation (X-band EPR). Under these conditions, sending photons of that energy would take any of these two states into the other while leaving the other two states unaffected (Fig. 12, right), which represents the implementation of this logic operation. Intriguing related questions are the coherence and fidelity of these operations. In particular, it will be necessary to ascertain how the off-diagonal anisotropy terms, which ultimately determine the possibility of performing the gate operations and their rates, might affect the wavefunction after a sequence of gate

operations are performed on a given input state.[54] In view of these very interesting properties, other members of the lanthanide series are being investigated in detail, involving for example the selection of isotopes with zero nuclear spin. One particularly attractive prospect is the possibility of using the non-equivalence of both metal sites in this complex to make heterometallic systems. This would allow to better differentiate the control from the target qubits of a CNOT QG, and choose the metals that would better fulfil either one or the other function.

7 Conclusions and outlook

This review shows that the versatility of coordination chemistry adds to the advantages of using electronic spins within molecules to carry out qubits and embody QGs for QIP. The examples shown here from different laboratories demonstrate that the same goals can be addressed via a variety of approaches. Clearly, the possibility of using coordination molecules as hardware for QC is still remote. However, we have shown here that significant progress has been made, including the experimental demonstration of suitable decoherence times, the capacity of devising ways to ensemble various types of cluster nanomagnets as pairs within molecules, or the possibility of generating an energy scheme potentially addressable for the realization of a CNOT logic operation. The value of this compilation is not only to show what has been done but to hint what might be achieved. The challenges of the still utopic goal of implementing QIP using coordination magnetic complexes are huge, but the process will need to involve the capacity of organizing the molecules into devices, introducing mechanisms to tune and switch the interaction between different qubits or different parts of a QG or addressing or reading out the information codified in the qubits. The next decade will undoubtedly witness many spectacular developments of this multidisciplinary area which is emerging with force as a key topic in Nanotechnology.

Acknowledgements

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